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# Density functional theory studies of the adsorption of ethylene and oxygen on Pt(111) and Pt<sub>3</sub>Sn(111)

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Density functional theory, employing periodic slab calculations, was used to investigate the interactions of ethylene and oxygen with Pt(111) and Pt<sub>3</sub>Sn(111). The predicted energetics and structures of adsorbed species on Pt(111) are in good agreement with experimental data. The binding energies of  $\pi$ -bonded ethylene, di- $\sigma$ -bonded ethylene, and ethylidyne species are weaker on Pt<sub>3</sub>Sn(111) than on Pt(111) by 21, 31, and 50 kJ/mol, respectively. Hence, the electronic effect of Sn on the adsorption of ethylene depends on the type of adsorption site, with adsorption on three-fold site weakened more than adsorption on two-fold and one-fold sites. Oxygen atoms bond as strongly on Pt<sub>3</sub>Sn(111) as on Pt(111), and these atoms prefer to adsorb near Sn atoms on the surface. The addition of Sn to Pt(111) leads to a surface heterogeneity, wherein ethylidyne species prefer to adsorb away from Sn atoms and oxygen atoms prefer to adsorb near Sn atoms. Implications of this surface heterogeneity on hydrocarbon reaction selectivity on Pt-based catalysts are discussed.

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## I. INTRODUCTION

The adsorptive and catalytic properties of metal alloys are generally controlled by geometric (or ensemble) and electronic (or ligand) effects, e.g., Refs. 1, 2. Typically, both types of phenomena are observed simultaneously for alloy systems, which makes it difficult to elucidate separately the quantitative consequences of these effects. In recent years, computational methods using density functional theory (DFT) have progressed owing to advances in computational speed along with the development of new algorithms, e.g., Refs. 3, 4. These methods provide a means for investigating in a systematic manner the electronic effects of metal alloying. Accordingly, we have used DFT methods in the present paper to investigate the effects of adding tin to Pt(111) for the adsorption of C<sub>2</sub>H<sub>4</sub> and oxygen atoms.

Platinum-based materials are employed extensively as catalysts for the reforming of hydrocarbon streams in the production of petrochemicals and gasoline.<sup>5,6</sup> It has been shown that the modification of platinum-based materials with tin suppresses hydrogenolysis and isomerization reactions of paraffins, resulting in catalysts that exhibit high dehydrogenation selectivity (e.g., Refs. 7–16). Furthermore, it has been suggested that because of the oxophilic nature of tin, it may actively participate in catalytic reactions involving oxygen-containing reactants. For example, it has been shown that tin is a useful modifier in metal-catalyzed reactions such as se-

lective reduction of esters to alcohols,<sup>17–19</sup> hydrogenation of carboxylic acids to aldehydes,<sup>20</sup> hydrogenation of aldehydes to alcohols,<sup>21–24</sup> and CO oxidation.<sup>25</sup> Finally, Pt/Sn catalysts have been studied for CO<sub>2</sub> reforming of methane,<sup>26</sup> and it has recently been reported that PtSn catalysts are effective for the oxidative dehydrogenation of ethane to ethylene.<sup>27</sup>

Various experimental investigations have studied the adsorption of C<sub>2</sub> hydrocarbons on single crystals of platinum as well as single crystals of platinum modified with tin. The results from these experimental studies show that the addition of tin to platinum leads to the formation of a substitutional alloy with platinum, thereby decreasing the number of three-fold hollow sites composed of adjacent Pt atoms which are necessary for the formation of ethylidyne species.<sup>28,29</sup> In addition to this geometric effect, there is evidence that tin also has an electronic effect on platinum. In particular, the interaction of Pt surface atoms with adsorbed hydrocarbon species appears to be weakened by the presence of neighboring Sn atoms.<sup>30–36</sup> For example, temperature programmed desorption (TPD) experiments show that desorption maxima are shifted to lower temperatures when Pt was alloyed with Sn.<sup>31,32</sup> Paffett and co-workers<sup>31</sup> have also found that the presence of Sn may alter the nature of the surface species formed on Pt. In this respect, the formation of ethylidyne species was suppressed on Pt–Sn surfaces, while di- $\sigma$ -bonded ethylene species formed to similar extents during ethylene adsorption on Pt(111) and Pt–Sn single crystal surfaces.

We have chosen in this paper to use ethylene as a probe molecule to study the interactions of metal and metal alloy surfaces with hydrocarbon species. We have used oxygen

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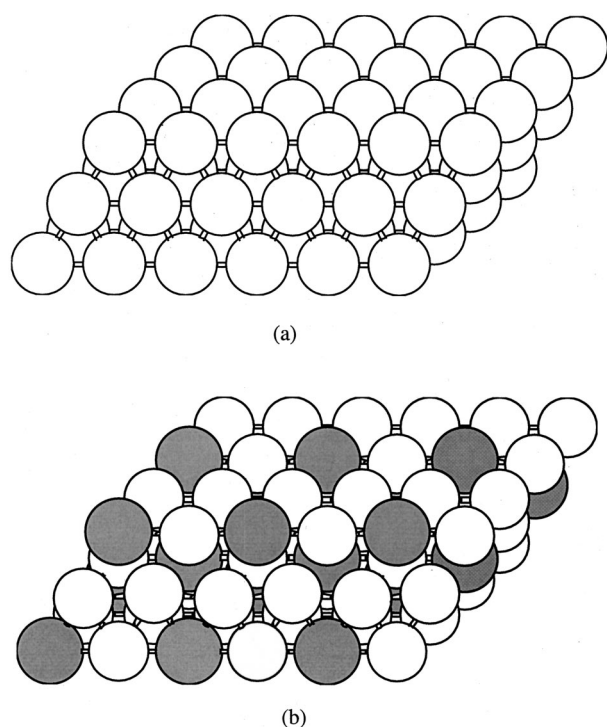


FIG. 1. Ball and stick models representing the periodic (a) Pt(111) and (b) Pt<sub>3</sub>Sn(111) slab, used for the calculations.

adsorption to probe interactions that may be relevant to understanding catalytic processes such as CO oxidation and NO<sub>x</sub> emissions control. We use periodic plane-wave calculations to study (111) surfaces of Pt and Pt<sub>3</sub>Sn. These calculations rigorously account for the electronic structure of a well-defined surface.

## II. COMPUTATIONAL DETAILS

We have primarily used three-layer slabs of Pt(111) and Pt<sub>3</sub>Sn(111) periodically repeated in a super cell geometry with four equivalent layers of vacuum between successive metal slabs, as shown in Fig. 1. The top metal layer for these three-layer slabs is allowed to relax along with the adsorbate in these calculations, while the bottom two layers are kept fixed at the calculated bulk lattice constant. (The errors in the adsorption energies introduced by using three-layer slabs are within 10 kJ/mol, as shown by representative calculations on four-layer slabs). The calculated equilibrium lattice constant for Pt is 4.00 Å. The corresponding experimental value is 3.92 Å.<sup>37</sup> The calculated equilibrium lattice constant for the Pt<sub>3</sub>Sn bulk alloy is 4.08 Å, while the experimental value is 4.00 Å.<sup>38</sup>

We have used a 2×2 unit cell to study the adsorption of various species, corresponding to  $\frac{1}{4}$  monolayer coverage. Adsorption occurs on one side of the slab. Ionic cores are described by ultrasoft pseudopotentials,<sup>39</sup> and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies below 25 Ry. The surface Brillouin zone is sampled at 18 special *k*-points. The exchange–correlation energy and potential are described by the generalized gradient approximation (PW-91).<sup>40,41</sup> The self-consistent PW-91 density is determined by iterative

diagonalization of the Kohn–Sham Hamiltonian, Fermi-population of the Kohn–Sham states ( $k_B T = 0.1$  eV), and Pulay mixing of the resulting electronic density.<sup>42,43</sup> Total energies have been extrapolated to  $k_B T = 0$  eV. Test calculations for the chemisorption of atomic oxygen showed no need to use the spin polarized version of the exchange–correlation functional.

## III. RESULTS AND DISCUSSION

### A. Pt(111) and Pt<sub>3</sub>Sn(111)

Figure 1 shows the three-layer slab used for periodic DFT calculations, consisting a total of 12 metal atoms in the supercell. To study the effect of Sn, we have replaced three Pt atoms in the supercell with Sn atoms one per layer of the slabs, as shown in Fig. 1. This Pt<sub>3</sub>Sn(111) slab exhibits the fcc *L*<sub>12</sub> structure similar to Cu<sub>3</sub>Au structure, with each (111) plane containing 25 at. % Sn. This type of structure is shown by Pt<sub>3</sub>Sn.<sup>44</sup> Previous studies have indicated that the (111) surface of the Pt<sub>3</sub>Sn alloy is the same as given by simple truncation of the bulk structure.<sup>44</sup> The Pt<sub>3</sub>Sn alloy is a stable compound with heat of formation equal to −42 kJ/mol.<sup>45</sup> The measured values of the work function of Pt(111) and the  $p(2 \times 2)$  surface of Pt<sub>3</sub>Sn(111) are 5.8 and 5.4 eV, respectively, indicating that the work function decreases with addition of Sn.<sup>46,47</sup> Our calculated values of the work function of Pt(111) and Pt<sub>3</sub>Sn(111) are 5.8 and 5.1 eV, respectively, in reasonable agreement with the experimental values.

We note that three-fold sites comprised of three adjacent Pt atoms are preserved on Pt<sub>3</sub>Sn(111) slabs. Hence, the DFT calculations probe the electronic effect of Sn atoms surrounding three-fold sites consisting of adjacent Pt atoms. Figure 2 shows schematic representations of the various adsorbates. The calculated values for the energetics of these species adsorbed on the Pt(111) and Pt<sub>3</sub>Sn(111) slabs are shown in Table I. It should be noted that several different types of two-fold and three-fold sites exist on Pt(111) and Pt<sub>3</sub>Sn(111), depending on the position of atoms in the second layer, e.g., three-fold sites with fcc versus hcp configurations. The results in Table I correspond to those sites that lead to the strongest bonding for a given adsorbate. The relative bonding strengths for different adsorption sites will be addressed below.

We calculate that the addition of Sn to Pt leads to an expansion of the lattice by 2.1%, in agreement with the experimental value of 2.0%.<sup>38</sup> Bardi and co-workers have measured the outward buckling of Sn on the surface of Pt<sub>3</sub>Sn(111) to be  $0.21 \pm 0.08$  Å with reference to the plane passing through the platinum atoms,<sup>38</sup> and we have calculated this value to be 0.19 Å. In general, the platinum atoms bonded to the adsorbate move upward upon adsorption, while the rest of the platinum or tin atoms move downward toward the metal slab.

### B. Ethylene on Pt(111) and Pt<sub>3</sub>Sn(111)

Various theoretical studies have addressed the adsorption of ethylene on platinum.<sup>48–55</sup> Table II shows a comparison of the calculated energetics and structural data with the corresponding experimental values. It has been shown that

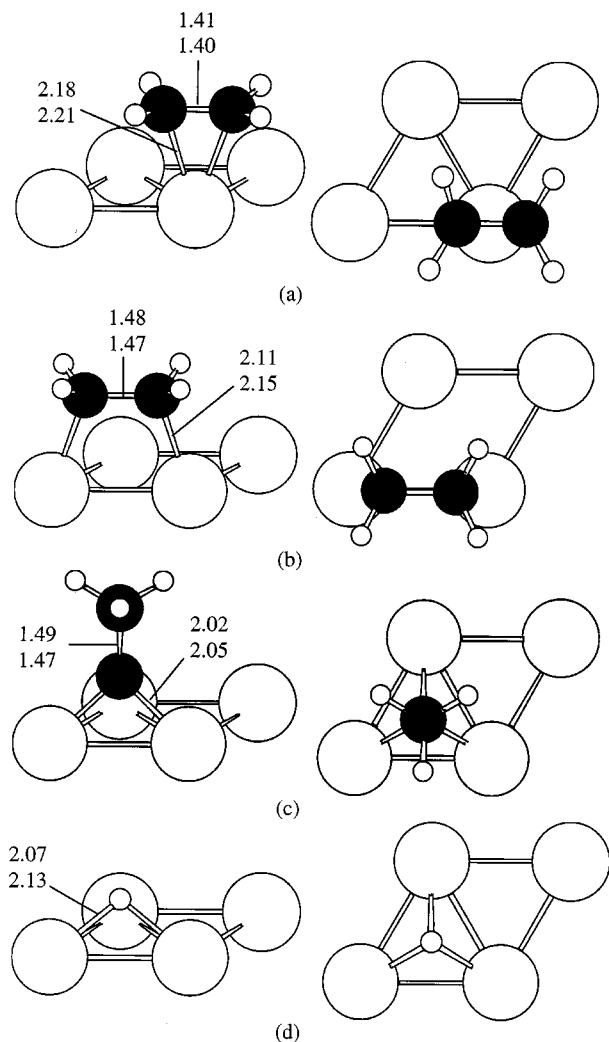


FIG. 2. Side and top views for adsorption of (a)  $\pi$ -bonded ethylene on an atop site, (b) di- $\sigma$ -bonded ethylene on a bridge site, (c) ethylidyne species on a three-fold site, and (d) oxygen in a three-fold site. Bond lengths are in Angstroms. The top and bottom numbers correspond to values on Pt(111) and Pt<sub>3</sub>Sn(111), respectively.

ethylene adsorbs as  $\pi$ -bonded species at low temperature and rehybridizes into di- $\sigma$ -bonded ethylene on Pt(111) at temperatures above 52 K.<sup>56,57</sup> This observation is in accord with the DFT result that di- $\sigma$ -bonded ethylene is more stable than  $\pi$ -bonded ethylene. Experimental studies of the interactions of ethylene with Pt(111) at temperatures above 280 K indicate that ethylene adsorbs dissociatively and rearranges such that the C-C axis is oriented perpendicular to the surface.<sup>58</sup> The resulting ethylidyne species prefers the three-fold site on Pt(111). The bonding energetics at the hcp and fcc three-fold sites are equivalent, as shown in Fig. 3.

The energy changes for adsorption of ethylene to form  $\pi$ -bonded ethylene, di- $\sigma$ -bonded ethylene and ethylidyne species on Pt(111) are -73, -117, and -95 kJ/mol, respectively. The corresponding values on Pt<sub>3</sub>Sn(111) are -52, -86, and -45 kJ/mol, respectively. Therefore, values on Pt<sub>3</sub>Sn(111) are weaker than on Pt(111) by 21, 31, and 50 kJ/mol, respectively. The weakening of the interaction of Pt surface atoms with adsorbed hydrocarbon species upon al-

TABLE I. Calculated changes in electronic energies (kJ/mol) for adsorption of ethylene and oxygen on Pt(111) and Pt<sub>3</sub>Sn(111) slabs.

Reaction <sup>a</sup>	Pt(111)	Pt <sub>3</sub> Sn(111)	Difference
$C_2H_4 + * \rightleftharpoons *C_2H_4(\pi)$	-73	-52	21
$C_2H_4 + * \rightleftharpoons *C_2H_4(di-\sigma)$	-117	-86	31
$C_2H_4 + * \rightleftharpoons *CCH_3 + 1/2H_2$	-95 <sup>b</sup>	-45 <sup>c</sup>	50
$2* + O_2 \rightleftharpoons 2*O$	-204	-204	0

<sup>a</sup>The \* denotes either the Pt(111) or Pt<sub>3</sub>Sn(111) surface. The negative values in the first two columns correspond to an exothermic reaction.

<sup>b</sup>The corresponding energy for four-layer slab is also -95 kJ/mol.

<sup>c</sup>The corresponding energy for four-layer slab is -38 kJ/mol.

loying with Sn has been observed in experimental studies.<sup>30-36,59</sup>

The electronic effect of tin on the adsorption of ethylene depends on the type of adsorption site. This dependence has important implications in the observed hydrocarbon chemistry on PtSn alloy catalysts. For example, we have recently combined results from experimental and theoretical investigations to interpret the observed reaction kinetics data for ethane hydrogenolysis over platinum,<sup>55,60,61</sup> which has been a probe reaction to investigate the reactivities of hydrocarbons over metal catalysts.<sup>62</sup> In our studies, we conclude that the preferred reaction pathways for cleavage of C-C bond involve activated  $C_2H_5$  and  $CHCH_3$  species, which occupy two-fold and three-fold sites, respectively. Upon addition of Sn, we predict that the activation barrier for the pathway over a three-fold site should be increased more than the pathway over a two-fold site. In agreement with these calculations, the observed catalytic activity of PtSn catalysts is lower than for Pt catalysts. We have also investigated isobutane dehydrogenation on Pt and PtSn catalysts.<sup>14,16,63</sup> The PtSn catalysts are more selective for dehydrogenation than Pt catalysts, since Sn inhibits isomerization, hydrogenolysis, and coking reactions. These latter reactions are generally believed to require multi-fold sites, at which our DFT calculations show that hydrocarbon species bond more weakly on PtSn compared to Pt.

Figures 3 and 4 show the calculated energies of adsorption of ethylidyne species on fcc (site A) and hcp sites (site D) comprised of three adjacent Pt atoms on Pt(111) and Pt<sub>3</sub>Sn(111) surfaces. We note that on the Pt<sub>3</sub>Sn(111) surface, the hcp three-fold site has an underlying Sn atom. Ethylidyne species do not differentiate between these two sites on a Pt(111) surface, while they show a strong preference toward the hcp site on the Pt<sub>3</sub>Sn(111) surface. Also, ethylidyne species do not adsorb strongly on three-fold sites containing a Sn atom. This reduction in the number of sites available for adsorption is a geometric effect of alloying an inactive metal like Sn with an active metal like Pt. In addition, our calculations show that Sn significantly weakens the bonding of ethylidyne species at three-fold sites (sites B, C) containing three Pt atoms, which is an electronic effect. Thus it appears that the addition of Sn to Pt(111) simultaneously leads to geometric and electronic effects for the adsorption of ethylidyne species. Moreover, both of these effects are unfavorable for adsorption of ethylidyne species. Therefore, it appears that Sn is a particularly effective agent for suppressing the



TABLE II. Comparison with experimental data of calculated energetics and structures of adsorbed species on Pt(111).

Reaction <sup>a</sup>	Energy Change (kJ/mol)		C–C distance (Å)	
	Calculated	Experimental	Calculated	Experimental
* + C <sub>2</sub> H <sub>4</sub> = *C <sub>2</sub> H <sub>4</sub> ( $\pi$ )	–73	–40 <sup>b</sup>	1.41	1.41 <sup>c</sup>
* + C <sub>2</sub> H <sub>4</sub> = *C <sub>2</sub> H <sub>4</sub> (di- $\sigma$ )	–117	–136, <sup>d</sup> –120 <sup>e</sup>	1.48	1.48–1.52 <sup>f</sup>
2* + C <sub>2</sub> H <sub>4</sub> = *CCH <sub>3</sub> + *H	–139	–174, <sup>g</sup> –160 <sup>h</sup>	1.49	1.50 <sup>i</sup>
2* + O <sub>2</sub> = 2*O	–204	–160––190 <sup>j</sup>		

<sup>a</sup>The \* denotes the Pt(111) surface. The negative values in the first two columns correspond to an exothermic reaction.

<sup>b</sup>From Ref. 79.

<sup>c</sup>From Ref. 80.

<sup>d</sup>From Ref. 81.

<sup>e</sup>From Ref. 82.

<sup>f</sup>From Refs. 83, 84.

<sup>g</sup>From Ref. 85.

<sup>h</sup>From Ref. 82.

<sup>i</sup>From Ref. 86.

<sup>j</sup>From Refs. 69, 87, 88.

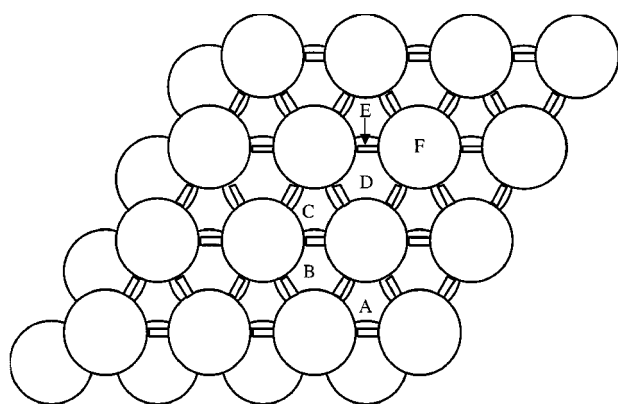
formation of ethylidyne species on Pt, since the geometric and electronic effects work in the same direction.

It has been shown previously that the coupling of adsorbate states with metal *d*-electrons gives rise to trends in binding energies.<sup>64,65</sup> The calculated *d*-band centers for Pt(111) and Pt<sub>3</sub>Sn(111) are –2.50 and –2.56 eV below the Fermi level, respectively. From Fig. 5(a), we note that ethylidyne species bond more weakly on all sites on Pt<sub>3</sub>Sn(111) compared to Pt(111), in agreement with the lower *d*-band center of the Pt<sub>3</sub>Sn(111). However, we note that the strong preference of the hcp site compared to the fcc site on Pt<sub>3</sub>Sn(111) cannot be explained by the *d*-band center position alone, since the *d*-band center is the same for both sites. Site preferences generally depend not only on the *d*-band center but

also on the band shape.<sup>66</sup> A more detailed analysis of this aspect of the problem will be presented elsewhere.<sup>67</sup>

### C. Oxygen on Pt(111) and Pt<sub>3</sub>Sn(111)

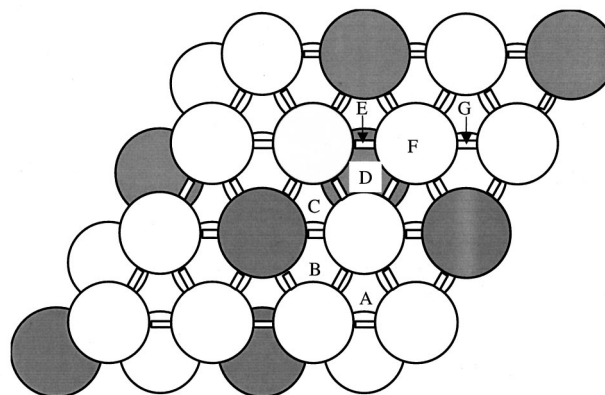
The most stable location for oxygen atoms on Pt(111) is the fcc three-fold site, in agreement with previous experimental and theoretical studies. The calculated height of oxygen atoms above the Pt(111) surface is 1.18 Å, in agreement with a LEED study which reported a value of 1.19 Å.<sup>68</sup> The calculated energies of dissociative adsorption of dioxygen are –204 and –120 kJ/mol on fcc and hcp three-fold sites, respectively. Since the calculated bond energy for gas phase dioxygen dissociation is 542 kJ/mol, the corresponding bind-



Pt(111)

Reaction	Adsorption Site			
	A (fcc)	D (hcp)	E (bridge)	F (top)
C <sub>2</sub> H <sub>4</sub> + * ⇌ *C <sub>2</sub> H <sub>4</sub> ( $\pi$ )				–73
C <sub>2</sub> H <sub>4</sub> + * ⇌ *C <sub>2</sub> H <sub>4</sub> (di- $\sigma$ )			–117	
C <sub>2</sub> H <sub>4</sub> + * ⇌ *CCH <sub>3</sub> + 1/2 H <sub>2</sub>	–95	–95		
2* + O <sub>2</sub> ⇌ 2*O	–204	–120		

FIG. 3. Schematic diagram of various adsorption sites available on Pt(111) and the corresponding changes in energies upon adsorption (kJ/mol).

Pt<sub>3</sub>Sn(111)

Reaction	Adsorption Site						
	A	B	C	D	E	F	G
C <sub>2</sub> H <sub>4</sub> + * ⇌ *C <sub>2</sub> H <sub>4</sub> ( $\pi$ )						–52	
C <sub>2</sub> H <sub>4</sub> + * ⇌ *C <sub>2</sub> H <sub>4</sub> (di- $\sigma$ )					–86		–66
C <sub>2</sub> H <sub>4</sub> + * ⇌ *CCH <sub>3</sub> + 1/2 H <sub>2</sub>	–11	41	34	–45			
2* + O <sub>2</sub> ⇌ 2*O	–62	–120	–204	–98			

FIG. 4. Schematic diagram of various adsorption sites available on Pt<sub>3</sub>Sn(111) and the corresponding changes in energies upon adsorption (kJ/mol). Gray circles represent the Sn atoms.

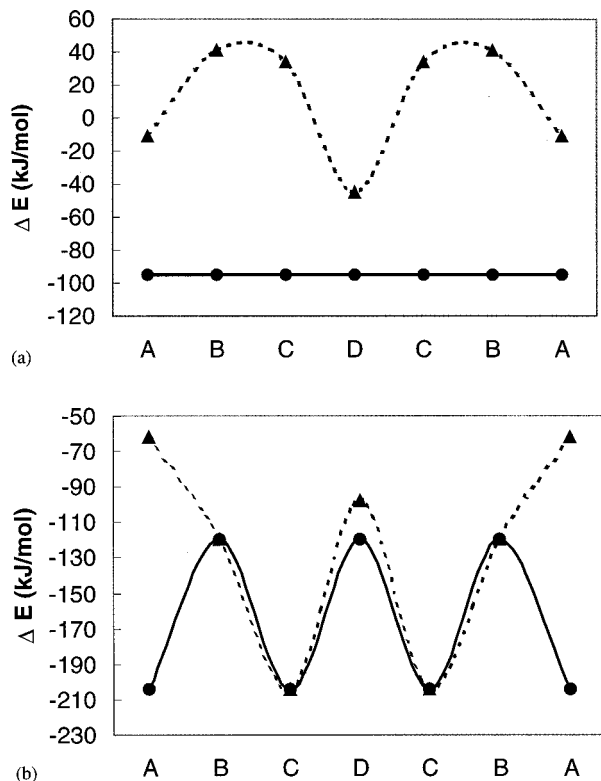


FIG. 5. The tin induced heterogeneity in the adsorption strengths: (a) energy change upon adsorption of ethylene to form gas phase dihydrogen and ethylidyne species, and (b) energy change upon dissociative adsorption of dioxygen, on Pt(111) (continuous line) and Pt<sub>3</sub>Sn(111) (dashed line). A, B, C, and D refer to site labels, as given in Figs. 3 and 4.

ing energies for oxygen atoms at fcc and hcp three-fold sites are calculated to be  $-373$  and  $-331$  kJ/mol, respectively. We have calculated that oxygen atoms bond significantly more strongly (by 50 kJ/mol) at a coverage of 1/6 ML compared to 1/4 ML investigated in this study. This result is in agreement with results from microcalorimetric studies, which show a decrease in the heat of oxygen adsorption by 100 kJ/mol from zero to 1/4 ML oxygen coverage.<sup>69</sup> Several theoretical studies using slab approaches have been performed to investigate the interactions of oxygen atoms on Pt(111).<sup>64,70–77</sup> Previous theoretical studies have predicted that adsorption of oxygen atoms is favored by 48 kJ/mol<sup>73</sup> and 64 kJ/mol<sup>71</sup> at the fcc three-fold site compared to the hcp three-fold site, in agreement with the difference of 42 kJ/mol calculated in the present study. Bleakley and Hu calculated the binding energy of atomic oxygen to be  $-428$  kJ/mol.<sup>75</sup>

Adsorption of oxygen atoms on Pt<sub>3</sub>Sn(111) is favored at an fcc three-fold site (site C) consisting of one tin atom and two platinum atoms, as shown in Fig. 4. The calculated energy of dissociative dioxygen adsorption is  $-204$  kJ/mol, which is same as that calculated for fcc three-fold sites on Pt(111). A recent TPD study of Pt/Sn alloys oxidized by ozone indicates that the activation energy for O<sub>2</sub> desorption increases from 210 kJ/mol on Pt(111) to 280 kJ/mol on Pt<sub>3</sub>Sn(111) at low oxygen coverages ( $<0.3$ ).<sup>78</sup> The difference in the desorption energies was attributed to the difference in Pt–O and Sn–O bond strengths, which were calculated to be 334 and 531 kJ/mol, respectively.<sup>78</sup>

From Fig. 5(b) we see that oxygen atoms bind more weakly at three-fold sites containing three Pt atoms (site A) on Pt<sub>3</sub>Sn(111) than on Pt(111), in agreement with the lower  $d$ -band center of Pt<sub>3</sub>Sn(111). However, we note that the favorable Sn–O interaction compensates for the decrease in bonding energy caused by the lower  $d$ -band center of Pt, and oxygen atoms thus bind as strongly on Pt<sub>3</sub>Sn(111) as on Pt(111) (site C). In general, we find that oxygen atoms prefer to adsorb near Sn atoms on the surface, while ethylidyne species prefer to adsorb away from Sn atoms on the surface. This arrangement suggests a favorable situation for coadsorption of the two species, since each species prefers to adsorb on a different type of site.

#### IV. CONCLUSIONS

We have investigated the electronic effects of adding Sn to Pt(111) on the binding energies of ethylene and oxygen. The decrease in the binding energy of ethylene on Pt<sub>3</sub>Sn(111) compared to Pt(111) depends on the type of adsorption site. This decrease is most significant for adsorption at three-fold sites (ethylidyne species), followed by two-fold sites (di- $\sigma$  bonded ethylene), and one-fold sites ( $\pi$ -bonded ethylene). Overall, tin appears to be a particularly effective agent for suppressing the formation of ethylidyne species on Pt. On the other hand, oxygen atoms prefer to segregate near Sn centers on the Pt<sub>3</sub>Sn(111) surface. Furthermore, oxygen atoms bind as strongly on Pt<sub>3</sub>Sn(111) as on Pt(111). Accordingly, the addition of Sn to Pt(111) leads to a surface heterogeneity, wherein ethylidyne species prefer to adsorb away from Sn atoms and oxygen atoms prefer to adsorb near Sn atoms.

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